Oxidative Recession, Sulfur Release, and Al_2O_3 Spallation for Y-Doped Alloys

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Introduction

Current Al_2O_3 scale adhesion mechanisms hold that reactive element dopants, such as Y, operate as getters of sulfur impurity atoms, thus preventing sulfur interfacial segregation, oxide-metal bond weakening, and scale spallation. Supporting this view, many alloys have demonstrated dramatic, first-order improvements in scale adhesion, without doping, when the sulfur impurity is eliminated by various means, such as melt cleaning or hydrogen annealing. Recently, however, some sporadic, second-order interfacial spallation has been observed for a Y-doped superalloy Rene'N5, after long-term oxidization for 1000 1-hr cycles at 1150°C [1]. The degree of spallation was increased by water immersion [2]. This contrasts with the measurably improved adhesion for undoped Rene'N5 that had been desulfurized by hydrogen annealing. While both alloy versions should exhibit optimum adhesion, it appeared that sulfur removal may be superior to Y-doping for this alloy in some instances. The purpose of this note is to raise the possibility that finite amounts of sulfur retained in the Y-doped alloy may actually be released to the interface as the surface layers of the alloy are consumed by oxidation. A relationship between the amount of oxidation, the bulk sulfur content of the alloy, and the quantity of sulfur released (in terms of segregated monolayers) is derived. A few supporting examples of this phenomenon are cited in this paper. The characterization and testing of these and comparable alloys are discussed more fully in prior studies [1,2].

Experimental

Undoped and Y-doped (50 ppmw) Rene'N5 (Ni-8Co-7Cr-6.2Al-7Ta-5W-2Mo-3Re-0.2Hf) samples (0.3 x 1.3 x 2.5 cm) were polished to a 600 grit finish and oxidized for 1000 1-hr cycles at 1150°C in the as-received or H_2-annealed condition (1250°C for 100 hr). Hydrogen annealing reduced the sulfur content of the undoped alloy from 2.6 to 0.01 ppmw (GDMS), but did not reduce the bulk sulfur content of the doped sample, which remained at about 5 ppmw. However hydrogen annealing did reduce the carbon content of both the doped and undoped alloys from about 400-500 ppmw down to $\leq$100 ppmw. Scale spallation was monitored by weight change and visual observation. After the 500

and 1000 hr cycles, the samples were immersed in water for 1-4 hours to test for moisture-induced spallation, as observed previously for less adherent scales [3,4].

Results

The weight change behavior of the as-received undoped and Y-doped samples is shown in figure 1a. It is seen that the undoped sample lost a considerable amount of weight, beginning at very early times in the test, and reached a final weight loss of 40 mg/cm². The Y-doped sample exhibited a first order improvement in scale adhesion and lost only 0.8 mg/cm² at the end of testing. Some discontinous drops in weight occurred at 500 and 1000 hr, when the sample immersed in water exhibited additional second-order spallation (up to 1.5 mg/cm²), not typical of the rest of the test. Moisture-induced spallation also occurred for the undoped sample to some degree all through the test. Figure 1b shows the corresponding weight change for hydrogen annealed samples. More adherent behavior is evidenced by positive weight changes of about 1 mg/cm² at the end of the test and less severe discontinuous losses due to water immersion (<0.3 mg/cm²). Here the undoped sample shows excellent behavior because of the low sulfur content. However the Y-doped sample also shows second-order improvement due to hydrogen annealing in both the cyclic response and in the water immersion exposures. The doped alloy is representative of 8 others showing, on average, similar behavior [1,2].
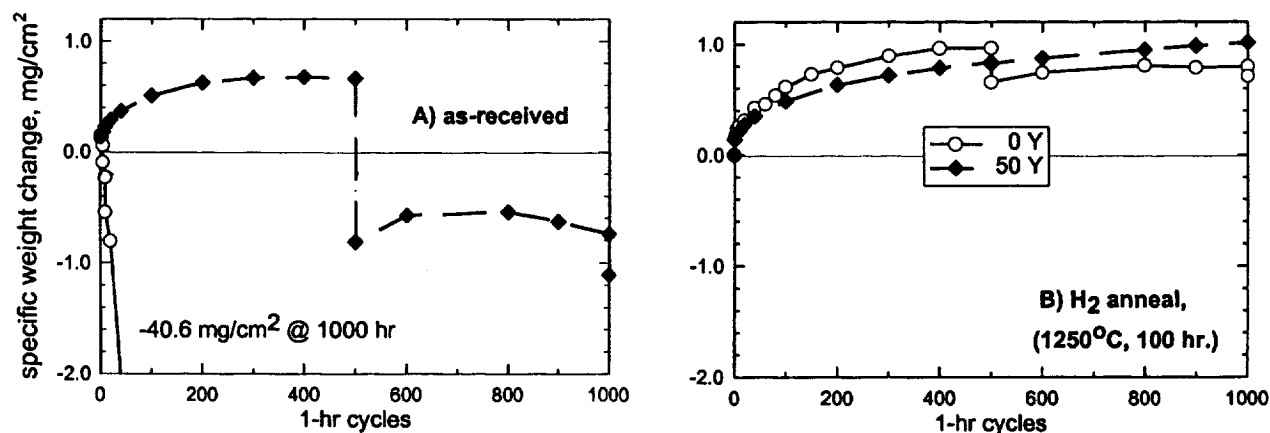

Figure 1. Cyclic oxidation weight change data for (A) as-received and (B) H₂-annealed
Rene'N5±Y at 1150°C in air; immersed in water at 500 and 1000 hr.

The interfacial spalling that occurred by immersion after 1000 hr of oxidation is summarized in Table 1 and exemplified by the optical macrographs in figure 2. Here the amount of spalling to bare metal is indicated by the reflective metallic surface area. For the as-received undoped sample, considerable spallation occurred from cycling, with a considerable increase in exposed metal area after immersion. In contrast, the hydrogen annealed undoped sample exhibited little indication of spalling due to cycling and a very small amount due to immersion. For the as-received Y-doped sample it is seen that an additional 15% of the surface area has spalled due to immersion, from a small initial amount of 0.4% . In contrast, the hydrogen annealed Y-doped sample exhibited little demonstration of spallation, even after immersion.

Sample	$\Delta W/A_{1000}$	$\Delta W/A_{H2O}$	$A_{s,1000}$	ΔA_{H2O}
Undoped	-40.642	-1.456 mg/cm²	5.15%	17.76 %
Undoped, (H₂)	0.797	-0.087	0.12	0.13
50 ppm Y	-0.742	-0.364	0.44	15.56
50 ppm Y, (H₂)	1.014	-0.027	0.01	- 0.01

Table 1. The effect of hydrogen annealing (H₂) and Y-doping on the final weight change, ΔW/A, and spalled area, A$_S$, after 1000 1-hr cycles at 1150°C for Rene'N5; additional losses after water immersion.

Thus the effect of Y-doping is seen to be first-order, as is the effect of hydrogen annealing, when compared to the as-received undoped condition. But also apparent are second-order effects caused by hydrogen annealing the Y-doped sample.
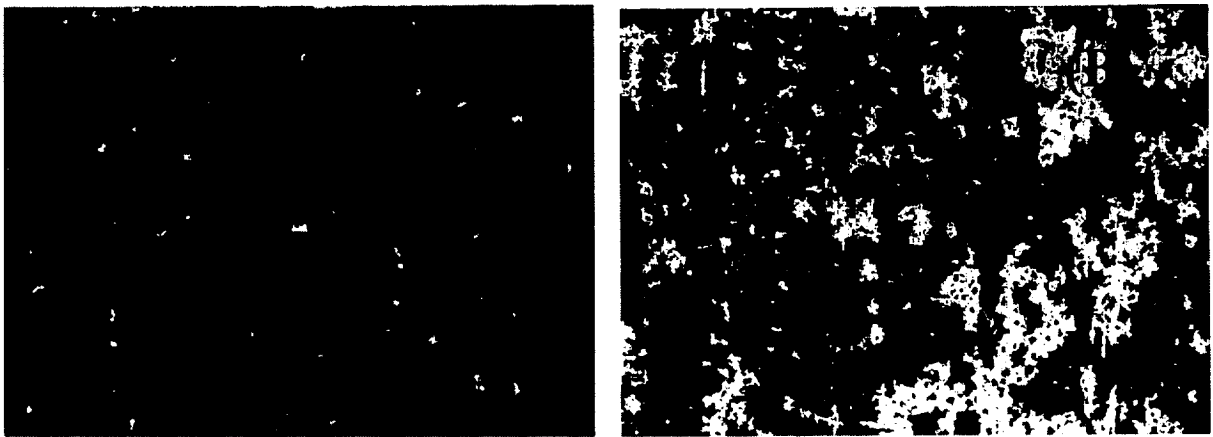

Figure 2. Effect of water immersion on surface spallation of as- received Y-doped Rene'N5, oxidized at 1150°C for 1000 1-hr cycles;   (A), as-cooled; (B) after water immersion.

Discussion

The first order effect of Y-doping is to dramatically increase scale adhesion and cyclic oxidation performance. However, it has been shown above that even in Y-doped Rene'N5, some interfacial spallation can be sustained after severe oxidation exposures. This spallation appears to be increased by moisture effects and reduced for alloys that were hydrogen annealed. Since these second-order effects are not easily explained by established precepts of scale adhesion, a modified perspective is offered. In this section an analysis is made of the amount of sulfur that is displaced by consumption of the Y-doped alloy surface due to oxidation. The proposal is that this amount of sulfur is now free to accumulate at the moving oxide-metal interface rather than be immobilized in the bulk by Y-dopants. If the accumulation rises to high enough values, second-order spallation events may be enabled intermittently over long periods of oxidation time.

The analysis is obtained from considering a representative cell of an oxidation sample volume and surface in figure 3. Here the oxidation area is A and the depth of alloy consumed by oxidation is x. The volume $V=A\,x$ is given by eqn. 1, where n_{Al} is the number of moles of aluminum consumed and $\delta V/\delta n_{Al}$ (i.e., V_{Al}) is the partial molal volume of aluminum in the alloy:

3

$$V = \int_0^t dn_{Al} \cdot \frac{\partial V}{\partial n_{Al}} \tag{1}$$

$$V = \int_0^t dn_{Al} \cdot \overline{V_{Al}} \tag{2}$$

The partial molal volume of Al in a Ni-20Cr-5Al was estimated to be 7.1 cm³/mole [5,6]. From the similarity of the NiCrAl alloy to the composition of Rene'N5 and only slight variations with composition, (molal volumes for pure Ni, Cr, and Al change only to 6.6, 7.2, and 10.0 cm³/mole), V_{Al} is approximated as a constant 7.1 cm³/mole value over the interval of integration, thus

$$V = A \cdot x = n_{Al} \cdot V_{Al} \tag{3}$$

The number of moles of aluminum reacted, n_{Al} is given by the weight of aluminum reacted divided by the atomic weight of aluminum. The weight of aluminum reacted per unit area is given by the oxygen weight gain per unit area, $\Delta W_O/A$, times the ratio of aluminum to oxygen weight in Al_2O_3. Thus:

$$x = \frac{54}{48} \cdot \left(\frac{\Delta W_o/A}{27\,gm/mole} \right) \cdot \left(7.1\,cm^3/mole \right) \tag{4}$$

$$x = 0.296\,(\Delta W_O/A)\,cm^3/gm \tag{5}$$

The amount of sulfur in the volume oxidized is given by the bulk sulfur concentration, C_S, in weight fraction, times the initial weight of this volume (given by $W_m = \rho_m \cdot A \cdot x$, where m refers to metal):

$$W_S = C_S \cdot W_m \tag{6}$$

$$W_S/A = C_S \rho_m x \tag{7}$$

Figure 3. Schematic oxidation cell of metal showing surface reaction area, A, and recession depth, x, for calculating the amount of sulfur released.
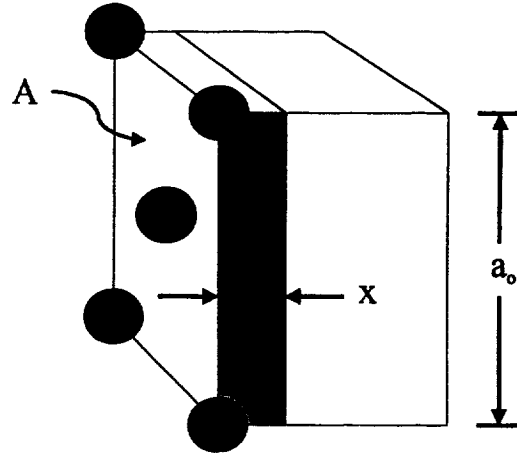
The amount of sulfur in this consumed volume is then assumed to be available for redistribution either in the bulk of the alloy or at the interface, i.e., not tied up by Y. Since it has been observed that Y and other oxygen-active elements migrate away from the alloy and into the scale or at the interface [7], it is reasonable to assume that Y-S complexes or particles do not simply retreat unaltered into the alloy

beneath the oxidation front. That is to say, there is evidence that Y-S bonding may indeed be disrupted in the layer consumed by oxidation. The interface is the most energetically favorable proximate and probable relocation site for sulfur, although some sulfur may be expected to diffuse back into the alloy if a thermodynamic excess of Y is also near the interface.

The next step is to draw the equivalence between the weight of sulfur per segregated monolayer, N_m, and the weight of sulfur in the consumed layer given by eqn.7. Considering an (001) layer of γ/γ' determined by XRD of Rene'N5, having two atom positions per (001) face with a lattice parameter of 3.580 Å, the number of atoms or sites per cm², N_{sites}/A, for one full monolayer is 1.56 x 10^{15}/cm². Thus the weight of interfacial sulfur per unit area is given by:

$$\frac{Ws}{A} = N_m \cdot \left(\frac{N_{sites}}{A}\right) \cdot \left(\frac{A.W._s}{N_{Av}}\right) \tag{9}$$

$$\frac{W_s}{A} = 8.31x10^{-8} \cdot N_m \left(\frac{gm}{cm^2}\right) \tag{10}$$

Finally, equating eqn's. 7 and 9 and substituting for x from eqn's. 3, then 5, with ρ_m =8.365 gm/cm³ measured for these Rene'N5 coupons:

$$N_m \cdot \left(\frac{N_{sites}}{A}\right) \cdot \left(\frac{A.W._s}{N_{Av}}\right) = C_S \cdot \rho_m \cdot \left(\frac{n_{Al}}{A}\right) \cdot \left(\overline{V_{Al}}\right) \tag{11}$$

$$N_m = 0.30 \times 10^8 \; C_S \; (\Delta W_o/A) \; cm^2/gm \tag{12}$$

Therefore, N_m = **0.03 for each 1 ppmw of S and for each 1 mg/cm² of oxygen reacted.** In the present example for Rene'N5 having 5 ppmw S and reacting with about 1 mg/cm² of oxygen, the total potential amount of segregated sulfur is equivalent to 0.15 monolayers. This is compared to surface saturation values of 0.5 monolayer for sulfur on nickel and measured values of 0.37 on undoped NiCrAl and about 0.25 on undoped PWA 1480 [8-10]. Since alumina scale spallation was quite apparent on the latter two alloys, it is not unreasonable to expect some spallation for conditions enabling 0.15 monolayer segregation. Furthermore, adhesion behavior was determined as a function of bulk sulfur content for PWA 1480 in 1100°C cyclic tests [11]. Here the total bulk sulfur equivalent of only 1 monolayer of segregation was sufficient to transition the material into primarily non-adherent scale behavior each cycle.

It should be emphasized that the thicker scales that spalled here only after 500 and 1000 hours exhibited high levels of stored strain energy. Audible pings were noticed and acoustic emission was recorded during spallation of these scales [2]. Creep and stress relaxation effects may be expected to be much less for these strong superalloys as compared to ductile FeCrAl alloys that are known to deform during oxidation and thus relax stresses [12,13]. Therefore some sporadic spallation may be expected. This is in contrast to undoped alloys with the same sulfur content that spall more profusely each cycle and thus sustain only limited scale growth.

It is also emphasized that this analysis is only offered as a possible or perhaps partial explanation of why Y-doped Rene'N5 can exhibit occasional second-order interfacial spallation under conditions of high strain energy in the scale and high levels of moisture. No direct confirmation of released sulfur

was obtained in this study, however it is not unusual to detect some surface sulfur segregation (5%), in hot stage Auger studies of doped NiCrAlY alloys [14].

Some improvement in adhesion was produced by hydrogen annealing the Y-doped alloy, even though sulfur was not measurably removed from this alloy [1,2]. It may be possible that a small amount of surface-mobile sulfur was removed by hydrogen annealing, undetected by bulk chemical analysis. The potential effect of carbon has also been noted, since this was the only element that decreased during hydrogen annealing for both doped and undoped alloys [1,2,15]. It has been suggested that decarburization and dissolution of Hf-carbides may allow the reactive element Hf to become more effective as a sulfur getter [1], but definite carbon effects remain unproven. Finally, even the sulfur-free (0.01 ppmw) hydrogen annealed undoped alloy exhibited some moisture-induced spallation after 500 hr, though by some criteria it showed better adhesion than doped alloys. Thus, second-order spallation behavior may be a borderline tendency for this alloy in any condition. High strain energy and moisture appear to be requirements for second-order spallation, with additional contributions possible from the sulfur released from the surface layer consumed by oxidation.

Summary

Second-order spallation phenomena have been noted for Y-doped Rene'N5 after long term oxidation at 1150°C. The reason for this behavior has not been conclusively identified. A mass equivalence analysis has shown that the surface recession resulting from oxidation has the potential of releasing about 0.15 monolayer of sulfur for every 1 mg/cm^2 of oxygen reacted for an alloy containing 5 ppmw of sulfur. This amount is significant in comparison to levels that have been shown to result in first-order spallation behavior for undoped alloys. Oxidative recession is therefore speculated to be a contributing source of sulfur and second-order spallation for Y-doped alloys.

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